

PATENT SPECIFICATION

(11) 1 571 199

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- (21) Application No. 41043/76 (22) Filed 4 Oct. 1976
 (31) Convention Application No. 619081
 (32) Filed 2 Oct. 1975 in
 (33) United States of America (US)
 (44) Complete Specification published 9 July 1980
 (51) INT CL³ B05D 5/00
 (52) Index at acceptance

B2E 1705 1706 419S 421S 438U 489CT ANA



(54) METHOD OF BONDING A SILICONE ELASTOMER TO A POROUS SUBSTRATE

(71) We, SWS SILICONES CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of Adrian, Michigan 49221, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

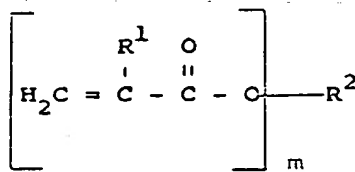
The present invention relates to a method of bonding a silicone elastomer to a porous substrate of a carbonaceous or masonry material, and to an article produced by bonding a silicone elastomer to a porous substrate according to the said method.

Silicone elastomers may be bonded to various substrates by first coating the substrate with a primer, then applying onto the coating of the primer an organopolysiloxane composition curable to a silicone elastomer and, finally, curing the organopolysiloxane composition. Various classes of silanes have been used in primers for this purpose including, for example, alkoxysilanes, alkylacyloxysilanes, alkylalkoxysilanes, alkoxyacyloxysilanes and vinyltriacyloxysilanes. Specific examples of silanes that have been used for this purpose are, for example, tetraethoxysilane, t-butoxytriethoxysilane, methyltriethoxysilane, methyltriacetoxysilane, ethyltriacetoxysilane and propyltriacetoxysilane. Although primers containing such silanes generally give good adhesion between silicone elastomers and metallic substrates, the degree of adhesion achieved when the substrate is porous and non-metallic is often inadequate, especially when the adhesive bond is subjected to high humidity or is in direct contact with water.

The present invention provides a method of bonding a silicone elastomer to a porous substrate of a carbonaceous or masonry material, which comprises applying to a surface of the substrate a primer composition that has been manufactured by causing a hydrocarbyl acrylate or a hydrocarbyl substituted acrylate to react with an (acryloyloxyhydrocarbyl)hydrocarbyloxysilane or a (substituted-acryloyloxyhydrocarbyl)hydrocarbyloxysilane in the presence of a free-radical initiator and an organic solvent, drying the primer composition by evaporation of the organic solvent, subsequently applying to the said surface an organopolysiloxane composition curable at room temperature to a silicone elastomer, and curing the organopolysiloxane composition.

For convenience, the term "acrylate" and derivatives thereof such as "acryloyl" will hereinafter be used to include "substituted acrylate" (e.g. methacrylate) and substituted derivatives thereof, respectively, except where the context obviously requires otherwise. Also for convenience, the (optionally substituted-acryloyloxyhydrocarbyl)hydrocarbyloxysilane will hereinafter be referred to as "the silane".

The acrylate used in the manufacture of the primer composition may be of the general formula



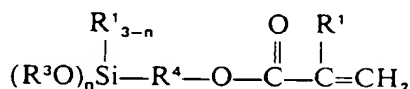
in which R¹ denotes a hydrogen atom or a monovalent hydrocarbon radical having up to 10 carbon atoms and either R² denotes a divalent hydrocarbon radical having

up to 10 carbon atoms and m denotes 2 or, preferably, R^2 denotes a monovalent hydrocarbon radical having up to 10 carbon atoms and m denotes 1.

Examples of monovalent hydrocarbon radicals denoted by R^1 and R^2 are especially alkyl radicals, for example, methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl and decyl radicals; and also aryl radicals, for example, phenyl and naphthyl radicals; alkaryl radicals, for example, tolyl, xylyl, cumenyl and ethylphenyl radicals and aralkyl radicals, for example, benzyl, α -phenethyl, β -phenethyl and α -phenylbutyl radicals. Examples of divalent hydrocarbon radicals denoted by R^2 are ethylene, trimethylene, tetramethylene, hexamethylene and octamethylene radicals.

An alkyl acrylate is preferably used as the acrylate, for example, methyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobutyl methacrylate and, especially, ethyl acrylate. Examples of suitable polyfunctional acrylates (*i.e.* acrylates having at least two unconjugated olefinic double bonds) are allyl methacrylate, allyl acrylate, 2-methylallyl acrylate, 2-methylallyl methacrylate, vinyl acrylate, vinyl methacrylate, ethylene dimethacrylate, tetramethylene diacrylate and 1,3-butylene dimethacrylate.

The silane used in the manufacture of the primer composition may be of the general formula



in which R^1 is defined as above, R^3 denotes a monovalent hydrocarbon radical having up to 10 carbon atoms, R^4 denotes a divalent hydrocarbon radical having from 2 to 10 carbon atoms, and n denotes 1, 2 or 3.

Examples of monovalent and divalent hydrocarbon radicals denoted, respectively, by R^3 and R^4 are those radicals listed above as examples of radicals denoted by R^1 and R^2 .

The silane is advantageously an (acryloyloxyalkyl)alkoxysilane or, especially a (methacryloyloxyalkyl)trialkoxysilane, for example, (methacryloyloxyethyl)trimethoxysilane, (methacryloyloxybutyl)trimethoxysilane, (methacryloyloxyhexyl)trimethoxysilane, (methacryloyloxyethyl)triethoxysilane, (methacryloyloxyethyl)tributoxysilane, (methacryloyloxyethyl)dimethoxybutoxysilane, (methacryloyloxyethyl)dibutoxymethoxysilane or, especially, (methacryloyloxypropyl)trimethoxysilane. Advantageously, at least one of the alkoxy groups in the (acryloyloxyalkyl)alkoxysilane has at least 3 carbon atoms, since this has been found to result in primer compositions having an improved stability.

A particularly preferred primer composition for use in the method according to the invention is one prepared from ethyl acrylate and (methacryloyloxypropyl)trimethoxysilane.

The free-radical initiator used in the manufacture of the primer composition is advantageously an organic peroxy compound, for example a compound of one of the formulae



in which formulae each R^5 denotes a monovalent organic radical. Suitable organic peroxy compounds are, for example, hydroperoxides, *e.g.* *t*-butyl hydroperoxide, cumene hydroperoxide and Decalin hydroperoxide ("Decalin" is a Trade Mark); dialkyl peroxides, *e.g.* di-*t*-butyl peroxide; diaralkyl peroxides, *e.g.* dicumyl peroxide; diacyl peroxides, *e.g.* benzoyl peroxide; cyclic peroxides, *e.g.* ascaridole; diperoxides, *e.g.* 2,5 - dimethyl - 2,5 - di - 5 - butyl peroxyhexane; peresters, *e.g.* *t*-butyl perbenzoate, *t*-butylperoxy isopropyl carbonate and *t*-butyl peroctoate; and keto peroxides, *e.g.* acetone peroxide and cyclohexanone peroxide.

Other free-radical initiators which may be used are, for example, azo compounds in which each azo nitrogen atom is attached to a tertiary carbon atom with the other bonds of each carbon atom attached to a cyano group, a carboxy group, a cycloalkyl group or an alkyl group, preferably having up to 18 carbon atoms.

The amount of free-radical initiator used may be any amount capable of producing a perceptible amount of free radicals and this will, of course, depend on the reactivity of the particular initiator chosen. Advantageously, the amount of

initiator used is within the range of from 0.01 to 1.0% by weight, but preferably at least 0.05% by weight, based on the acrylate and silane.

Especially when the initiator is a normally solid substance, it may be advantageous, in order to facilitate addition of the initiator to the reactants, first to dilute it with an inert solvent. Any solvent with a low chain-transfer activity is suitable for this purpose, for example benzene, toluene, xylene, chlorobenzene, cyclohexane and ethyl acetate. The concentration of the initiator in this solvent may be as low as 1% by weight, but is preferably within the range of from 5 to 20% by weight, based on the weight of the solvent.

The organic solvent used for carrying out the reaction between the acrylate and the silane is preferably a hydrocarbon or a halogenated hydrocarbon. The solvent may be, for example, an aromatic hydrocarbon, *e.g.* benzene, toluene or xylene; a halogenated aromatic hydrocarbon, *e.g.* chlorobenzene; an aliphatic hydrocarbon, *e.g.* pentane, hexane, octane or decane; a halogenated aliphatic hydrocarbon, *e.g.* methylene chloride, carbon tetrachloride or perchloroethylene; a ketone, *e.g.* methyl ethyl ketone; an ester, *e.g.* ethyl acetate; or an ether, *e.g.* diethyl ether or dibutyl ether. The solvent should preferably be one that will evaporate readily under the conditions under which the primer composition is to be applied to the substrate.

The reaction between the acrylate and the silane may be carried out at any temperature within the range of from room temperature to the reflux temperature of the organic solvent used. Advantageously, the reaction is carried out at a temperature within the range of from 50 to 150°C. It has been found particularly advantageous to carry out the reaction at such a temperature that the half-life of the initiator is within the range of from 15 min to 10 h, preferably from 1 to 6 h, and especially about 4 h. Table 1 lists the optimum reaction temperature ranges for various initiators. The first column in the table lists the various initiators, the second column indicates the temperature at which the respective initiator has a half-life of 4 h, and the third column indicates the preferred reaction temperature range when using the respective initiator.

TABLE 1

Initiator	Four-hour half-life temperature (°C)	Preferred temperature range (°C)
2,4-dichlorobenzoyl peroxide	61	60—75
azobisisobutyronitrile	73	70—85
benzoyl peroxide	79	75—90
t-butyl peroctoate	80	75—90
1,1-di-t-butylperoxy-3,3,5-trimethylcyclohexane	101	100—110
t-butylperoxy isopropyl carbonate	107	105—115
t-butyl perbenzoate	113	110—125
di-t-butyl peroxide	135	130—145

The molar ratio of the amount of acrylate to the amount of silane used in the manufacture of the primer composition may be from 1:99 to 99:1, advantageously from 5:95 to 95:5. The amount of organic solvent used is advantageously such as will give a solution containing a total of from 5 to 60% by weight, preferably from 10 to 50% by weight, of the acrylate and the silane, based on the total weight of the reactants and solvent.

The solution obtained from the reaction of the acrylate with the silane may be used directly as the primer composition for bonding the silicone elastomer to the porous substrate.

The method according to the invention is used for bonding a silicone elastomer to a porous substrate of a carbonaceous material or, especially, a masonry material.

The application of the primer composition to the surface of the substrate may be effected in any suitable conventional manner, for example, by spraying, dipping, brushing or wiping.

As indicated previously, the concentration of the primer solution is advantageously from 5 to 60%, preferably from 10 to 50%, by weight, based on the total weight of the reactants and solvent. It has been found that the greater is the

porosity of the substrate, the higher should be the concentration of the solution in order to achieve a good adhesion between the silicone elastomer and the substrate.

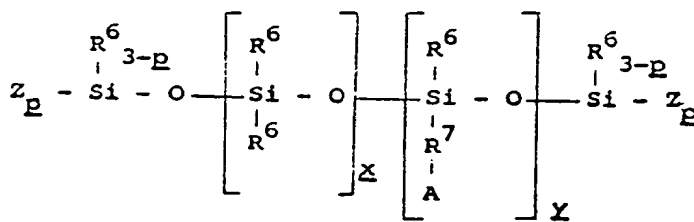
When the primer composition has been applied to the surface of the substrate, it is dried so as to leave a coating on the said surface. This drying entails evaporation of the organic solvent of the primer composition and may take from 10 seconds to several hours depending on the drying temperature and on the particular solvent used. Drying may be effected at any convenient temperature from ambient temperature to the boiling point of the solvent.

Room-temperature-vulcanisable (RTV) organopolysiloxane compositions, that is to say organopolysiloxane compositions that are curable at room or ambient temperature to silicone elastomers, are well known and may be of several types. In particular, such compositions may be "one-component compositions" or "two-component compositions".

One-component room-temperature-vulcanisable organopolysiloxane compositions have to be stored in the absence of air and moisture and, on access of air and/or moisture, will cure without the addition of a further component. These compositions generally contain silicon-bonded groups hydrolysable by atmospheric moisture. Two-component room-temperature-vulcanisable organopolysiloxane compositions, on the other hand, have to be stored as two separate components since curing will commence immediately on mixing the two components, irrespective of the presence or absence of air and moisture. The organopolysiloxanes used in these compositions need not contain groups susceptible to air or moisture.

The organopolysiloxane used in either type of composition may be a modified organopolysiloxane, that is to say an organopolysiloxane having one or more side chains or branches consisting of a carbon-to-carbon polymer. A modified organopolysiloxane may be prepared by graft-polymerising an organopolysiloxane with an aliphatically unsaturated monomer in the presence of a free-radical initiator: hydrogen is abstracted, by the initiator, from a silicon-bonded organic radical thus forming an active site for the grafting of the organic monomer and/or polymer. The manufacture of modified organopolysiloxanes is described in greater detail in, for example, U.S. Patent Specifications Nos. 3 555 109, 3 627 836, 3 631 087, 3 694 478 and 3 776 875. The term "organopolysiloxanes" as used hereinafter includes a modified organopolysiloxane except where the context obviously requires otherwise.

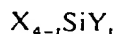
An organopolysiloxane suitable for use in a room-temperature-vulcanisable organopolysiloxane composition—that is in either a one-component composition or in a two-component composition—may be represented by the general formula



in which R^6 denotes a monovalent hydrocarbon or halogenohydrocarbon radical having up to 18 carbon atoms or a cyanoalkyl radical, R^7 denotes a divalent hydrocarbon or halogenohydrocarbon radical having up to 18 carbon atoms, A denotes an organic polymeric radical, Z denotes, in the case of a one-component composition, a hydroxy group or a group hydrolysable by atmospheric moisture or, in the case of a two-component composition, a hydroxy group, p denotes 1, 2 or 3, x denotes zero or an integer up to 20 000, and y denotes zero or an integer up to 500, with the proviso that the sum $x+y$ is not less than 10.

In addition to comprising an organopolysiloxane of the above general formula, an organopolysiloxane composition comprises a cross-linking agent.

A suitable cross-linking agent for use in a one-component organopolysiloxane composition—essentially if, in the above general formula, Z denotes a hydroxy group, but optionally if Z denotes a hydrolysable group—is a silane or siloxane containing at least three hydrolysable groups per molecule, for example a silane cross-linking agent of the general formula



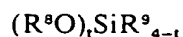
in which X denotes a group that is inert under the curing conditions, for example, an alkyl or aryl group, preferably having up to 8 carbon atoms, Y denotes a group hydrolysable by atmospheric moisture, for example, an acyloxy, oximo, alkoxy, aminoxy, amido, amino, halogeno or phosphato group, and *t* denotes 3 or 4. Examples of silanes of the above general formula are methyltriacetoxysilane, isopropoxytriacetoxysilane, methyltriacetoximosilane and methyltris(diethylphosphato)silane. The amount of the silane cross-linking agent of the above general formula in the composition is advantageously within the range of from 0.5 to 10%, preferably from 1 to 5%, by weight based on the organopolysiloxane.

Another suitable cross-linking agent for use in a one-component composition is an organo-hydrogenopolysiloxane of the average unit formula



in which R^6 is defined as above and *w* has a value between 0 and 2 exclusive.

A cross-linking agent suitable for use in a two-component organopolysiloxane composition is, for example, a (polyhydrocarbonoxy)silane of the general formula



or a partial hydrolysate thereof, or a (polyhydrocarbonoxy)siloxane in which any silicon valencies not satisfied by siloxane oxygen atoms are satisfied by a group denoted by $\text{R}^8\text{O}-$ or R^9 , in which formulae R^8 denotes a monovalent hydrocarbon radical having up to 8 carbon atoms, R^9 denotes a monovalent hydrocarbon or halogenohydrocarbon radical having up to 8 carbon atoms, and *t* denotes 3 or 4.

Examples of hydrocarbon radicals denoted by R^8 and R^9 are methyl, ethyl, propyl, butyl, hexyl, octyl, phenyl, vinyl, allyl and ethylallyl radicals. Examples of halogenohydrocarbon radicals denoted by R^9 are chloromethyl, 2-bromo-4,6-diiodophenyl, 1,2-difluorovinyl and 6-chlorohexyl radicals.

Such a cross-linking agent may be, for example, a monoorganotrihydrocarbonoxysilane, a tetrahydrocarbonoxysilane, or a partial hydrolysate thereof; an alkyl silicate, a polysilicate, or a partially hydrolysed silicate; or a siloxane. Particular examples of these cross-linking agents are ethyltrimethoxysilane, methylbutoxy diethoxysilane, propyltripropoxysilane, methyltriethoxysilane, ethyltriethoxysilane, tetraethyl orthosilicate, n-butyl orthosilicate, "ethyl silicate 40", ethyl polysilicates, isopropyl polysilicates, butyl polysilicates, trimethyltributoxydisiloxane and trimethylpentabutoxytrisiloxane.

The amount of such a cross-linking agent is advantageously from 0.5 to 20%, preferably from 1 to 10%, by weight based on the organopolysiloxane.

In a two-component organopolysiloxane composition, the organopolysiloxane and the cross-linking agent are stored separately and mixed immediately prior to use. Such a composition also comprises a curing catalyst which, when the composition is being stored, may be in admixture with either the organopolysiloxane or the cross-linking agent. Suitable curing catalysts are carboxylic acid salts of lead, tin, zirconium, iron, cadmium, titanium, calcium and manganese. Advantageously, the carboxylic acid radical has not more than 18, preferably not more than 16, carbon atoms. It is also preferred that the carboxylic acid salt be soluble in the organopolysiloxane. Carboxylic acid salts of tin are particularly preferred.

Specific examples of suitable curing catalysts are tin naphthenate, lead octoate, tin octoate, iron stearate, tin oleate, antimony octoate, tin butyrate, dibutyltin butoxychloride, dibutyltin dilaurate, bis - (dibutylphenyltin)oxide, bis - (acetoxydibutyltin)oxide, bis(tributyltin)oxide, dibutoxydibutyltin, *t* - butyltin hydroxide, triethyltin hydroxide, diamyldipropoxytin, dioctyltin dilaurate, diphenyloctyltin acetate, dodecyldiethyltin acetate, tricetyl tin acetate, triphenyltin acetate and tridecyltin laurate.

The curing catalyst may be dispersed in an organic liquid diluent and then be incorporated in the organopolysiloxane composition, or it may be mixed with a filler or other auxiliary and then be milled with the composition. Suitable liquids for dispersing the catalyst are hydrocarbons, for example, benzene, toluene and xylene; halogenohydrocarbons, for example, tetrachloroethylene and chlorobenzene; ethers, for example, diethyl ether and dibutyl ether; and hydroxy-free organopolysiloxane fluids. The liquid should advantageously be sufficiently volatile to evaporate at room temperature.

The amount of the curing catalyst is advantageously from 0.05 to 2%, preferably from 0.1 to 1%, by weight based on the organopolysiloxane composition.

The organopolysiloxane composition—be it a one-component composition or a two-component composition—may additionally comprise a filler and/or one or more other auxiliaries. Whether a filler and/or other auxiliaries are included in the composition and, if so, the amount and type thereof will depend on the intended use of the silicone elastomer to be produced from the composition. Examples of fillers that may be used are various silicas, for example, fumed silicas, high surface area precipitated silicas, silica aerogels and coarser silicas such as diatomaceous earth and crushed quartz; metallic oxides, for example, titanium oxide, ferric oxide and zinc oxide; and fibrous fillers, for example, asbestos and glass fibres. Other auxiliaries which may be used are, for example, pigments, antioxidants and ultraviolet absorbers.

The method of the invention can be used to produce a wide range of products by bonding, for example coating, silicone rubber onto porous substrates of masonry or carbonaceous material. Such products may be subjected to a water environment while still maintaining a good adhesive bond between the rubber and the substrate.

The following examples illustrate the method of the invention. All parts are by weight.

Example 1

A mixture of 9.7 parts of (methacryloyloxypropyl)trimethoxy silane, 81 parts of ethyl acrylate and 1.2 parts of di-t-butylperoxide were added, over a period of 6 h, to 90 parts of toluene heated to reflux temperature, after which refluxing was continued for an additional hour. An opaque viscous product was obtained which is applied, by brush, to a porous masonry substrate and dried at room temperature.

A room-temperature-vulcanisable organopolysiloxane composition containing 100 parts of a hydroxy-terminated dimethylpolysiloxane having a viscosity of about 4000 cSt at 25°C, 5 parts of methyltriacetoxysilane and 8 parts of Cab-O-Sil (Trade Mark) was applied to the dried substrate and cured in the presence of atmospheric moisture for 48 h. The coated masonry substrate was then immersed in water for 7 days, after which the adhesive bond was tested by trying to remove the silicone elastomer from the primed substrate. Excellent adhesion between the silicone elastomer and the masonry substrate was observed.

Example 2

Four primer compositions are prepared in accordance with the procedure of Example 1 but using 13 parts of (methacryloyloxypropyl)-trimethoxysilane, 48 parts of ethyl methacrylate and the amounts of toluene given in Table 2. The resultant compositions were each applied as a film to porous masonry substrates, dried and thereafter the room-temperature-vulcanisable organopolysiloxane composition described in Example 1 was applied thereto. The coated masonry substrates were each immersed in water for 7 days, after which time the adhesive bond was tested by trying to remove the silicone rubber from the primed substrate. The results of these tests are given in Table 2 as Examples 2(a) to 2(d).

In a comparative test, a porous masonry substrate was treated with a composition containing 30 parts of vinyltriacetoxysilane and 70 parts of toluene, dried and thereafter the room-temperature-vulcanisable organopolysiloxane composition described in Example 1 was applied thereto. The coated masonry substrate was immersed in water for 7 days, after which the adhesive bond was tested by trying to remove the silicone rubber from the primed substrate. The result is given in Table 2 as Example 2(e).

In another comparative test, a porous masonry substrate was coated with a composition containing 30 parts of vinyltriethoxysilane and 70 parts of toluene, dried and thereafter the room-temperature-vulcanisable organopolysiloxane composition described in Example 1 was applied thereto. After being cured for 48 hours at room temperature, the coated masonry substrate was immersed in water for 7 days, after which the adhesive bond was tested as described above. The result is given in Table 2 as Example 2(f).

In a similar test, the room-temperature-vulcanisable organopolysiloxane composition described in Example 1 was applied to an unprimed porous masonry substrate. After being cured for 48 hours at room temperature, the coated substrate was immersed in water for 7 days, after which the adhesive bond was tested by trying to remove the rubber from the primed substrate. The result is given in Table 2 as Example 2(g).

TABLE 2

	Example No.	Toluene (parts)	Adhesion	
	2(a)	122	Excellent	
	2(b)	244	Good	
5	2(c)	549	Fair	5
	2(d)	1159	Poor	
	2(e)*	70	None	
	2(f)*	70	None	
	2(g)*	0	None	

10 *indicates a comparison example. 10

Example 3

15 A composition prepared in accordance with Example 2(a) was applied to a porous masonry substrate and dried. A room-temperature-vulcanisable organopolysiloxane composition prepared by mixing 100 parts of a hydroxy-terminated dimethylpolysiloxane having a viscosity of about 10,000 cSt at 25°C with 8 parts of methyltris(cyclohexylamino)silane, 50 parts of a trimethylsiloxy-terminated dimethylpolysiloxane having a viscosity of 50 cSt at 25°C and 17 parts of diatomaceous earth was applied to the coated masonry substrate and exposed to atmospheric moisture for 48 h. The coated substrate was then immersed in water for 7 days, after which the adhesive bond was tested by trying to remove the rubber from the primed substrate. Excellent adhesion between the silicone elastomer and the substrate was observed. 20

Example 4

25 A primer composition was prepared by adding a mixture of 62 parts of butyl acrylate, 13 parts of (methacryloyloxypropyl)trimethoxysilane and 0.7 part of di-
butylperoxide to 75 parts of toluene. The reaction mixture was heated to reflux temperature and maintained at that temperature for 6 h. The product was cooled to room temperature, after which 100 parts of toluene were added. The product was then applied by brushing onto a porous masonry substrate and dried at room temperature. The room-temperature-vulcanisable organopolysiloxane composition described in Example 1 was applied thereto and cured at room temperature for 48 h. The coated masonry substrate was immersed in water for 7 days, after which the adhesive bond between the primed substrate and the silicone elastomer was tested. Good adhesion between the silicone and the primed substrate was observed. 30

Example 5

35 A primer composition was prepared in accordance with Example 4, except that 100 parts of tetramethylene diacrylate were used instead of the butyl acrylate and 190 parts of toluene were employed. The reaction product was applied to a concrete substrate and dried. The room-temperature-vulcanisable organopolysiloxane composition of Example 1 was applied to the coated substrate and cured at room temperature. The coated substrate was immersed in water for 7 days, after which time the adhesive bond was tested. Excellent adhesion between the silicone rubber and the coated substrate was observed. 40

Example 6

45 (a) A modified organopolysiloxane composition was prepared by heating a mixture of 80 parts of a hydroxy-terminated dimethylpolysiloxane (400 cSt at 25°C), 54 parts of butyl acrylate and 66 parts of styrene to 150°C with agitation. A solution containing 0.4 part of t-butylperbenzoate in 6 parts of toluene was added in increments of 0.3 part at intervals of 20 min. When the addition had been completed, the reaction mixture was heated at 150°C for an additional 30 min. 50
About 100 parts of the modified organopolysiloxane prepared above were mixed with 5 parts of "ethyl silicate 40" and 0.5 part of dibutyltin butoxychloride and applied to a porous masonry substrate coated with the primer composition of Example 1 and dried. The modified organopolysiloxane composition was cured at room temperature for 48 h and then immersed in water for 7 days. Excellent adhesion between the modified organopolysiloxane composition and the porous masonry substrate was observed. 55

60 (b) The procedure of Example 6 (a) was repeated except that a room-temperature-curable organopolysiloxane composition containing 5 parts of methyltriacetoxysilane, 100 parts of the modified organopolysiloxane prepared in

accordance with Example 6 (a) and 8 parts of Cab-O-Sil (Trade Mark) was applied to the coated masonry substrate. The organopolysiloxane composition was cured for 48 h, after which time the coated masonry substrate is immersed in water for 7 days. Excellent adhesion between the silicone elastomer and the porous masonry substrate was observed.

Example 7

A porous masonry substrate was primed with the composition of Example 1, dried and, thereafter, a room-temperature-vulcanisable organopolysiloxane composition containing 5 parts of "ethyl silicate 40", 100 parts of a hydroxy-terminated dimethylpolysiloxane having a viscosity of about 2000 cSt at 25°C, 0.5 part of dibutyltin dilaurate and 60 parts of iron oxide was applied thereto. The room temperature vulcanisable organopolysiloxane composition was cured at room temperature for 48 h, after which time the masonry substrate was immersed in water for 7 days. Excellent adhesion between the silicone rubber and the primed substrate was observed.

Example 8

In a comparison test, a composition was prepared by adding dropwise over a period of 30 min a mixture containing 90 parts of (methacryloyloxypropyl)trimethoxysilane and 0.9 part of di-t-butyl peroxide to 180 parts of toluene at reflux temperature. The reactants were refluxed for an additional 5 h, cooled and then applied to a concrete substrate. After drying overnight, the room-temperature-vulcanisable composition prepared in accordance with Example 1 was applied and cured in the presence of atmospheric moisture for 48 h. The coated substrate was then immersed in water for 7 days, after which time the adhesive bond between the silicone elastomer and the primed substrate was tested. Only slight adhesion between the silicone elastomer and the primed substrate was observed.

Example 9

In a comparison test, a composition was prepared by refluxing 50 parts of ethyl methacrylate, 0.5 part of t-butylperoxy isopropyl carbonate and 100 parts of toluene for about 6.5 h. The reaction mass is cooled and applied to a concrete substrate. After drying, a room-temperature-vulcanisable composition prepared in accordance with Example 1 was applied to the dried substrate and cured in the presence of atmospheric moisture for 48 h. The coated substrate was immersed in water for 7 days, after which time the adhesive bond between the silicone elastomer and the primed substrate was tested. No adhesion between the silicone elastomer and the primed substrate was observed.

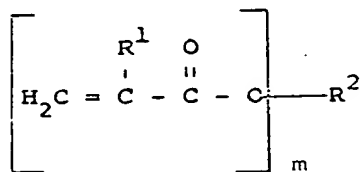
Example 10

The room-temperature-vulcanisable organopolysiloxane composition of Example 1 was applied to a carbon-black surface that had been primed with the primer composition of Example 1. Excellent adhesion of the silicone elastomer to the surface was observed even after being immersed in water for several days.

WHAT WE CLAIM IS:—

1. A method of bonding a silicone elastomer to a porous substrate of a carbonaceous or masonry material, which comprises applying to a surface of the substrate a primer composition that has been manufactured by causing a hydrocarbyl acrylate or a hydrocarbyl substituted acrylate to react with an (acryloyloxyhydrocarbyl)hydrocarbyloxysilane or a (substituted-acryloyloxyhydrocarbyl)hydrocarbyloxysilane in the presence of a free-radical initiator and an organic solvent, drying the primer composition by evaporation of the organic solvent, subsequently applying to the said surface an organopolysiloxane composition curable at room temperature to a silicone elastomer, and curing the organopolysiloxane composition.

2. A method as claimed in claim 1, wherein the acrylate is of the general formula



in which R¹ denotes a hydrogen atom or a monovalent hydrocarbon radical having up to 10 carbon atoms and either R² denotes a monovalent hydrocarbon radical having up to 10 carbon atoms and *m* denotes 1 or R² denotes a divalent hydrocarbon radical having up to 10 carbon atoms and *m* denotes 2.

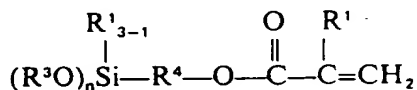
3. A method as claimed in claim 2, wherein, in the general formula given in claim 2, R¹ denotes an alkyl radical.

4. A method as claimed in claim 2 or claim 3, wherein, in the general formula given in claim 2, *m* denotes 1 and R² denotes an alkyl radical.

5. A method as claimed in claim 1, wherein the acrylate is an alkyl acrylate or an alkyl substituted acrylate.

6. A method as claimed in claim 1, wherein the acrylate is ethyl acrylate.

7. A method as claimed in any one of claims 1 to 6, wherein the silane is of the general formula



in which R¹ is defined as in claim 2, R³ denotes a monovalent hydrocarbon radical having up to 10 carbon atoms, R⁴ denotes a divalent hydrocarbon radical having from 2 to 10 carbon atoms, and *n* denotes 1, 2 or 3.

8. A method as claimed in claim 7, wherein, in the general formula given in claim 7, each of R¹ and R³ denotes an alkyl radical.

9. A method as claimed in any one of claims 1 to 6, wherein the silane is an (acryloyloxyalkyl)alkoxysilane or a (methacryloyloxyalkyl)trialkoxysilane.

10. A method as claimed in claim 9, wherein at least one of the alkoxy groups in the silane has at least 3 carbon atoms.

11. A method as claimed in any one of claims 1 to 5, wherein the silane is (methacryloyloxypropyl)trimethoxysilane.

12. A method as claimed in claim 1, wherein the acrylate is ethyl acrylate and the silane is (methacryloyloxypropyl)trimethoxysilane.

13. A method as claimed in any one of claims 1 to 12, wherein the initiator is an organic peroxy compound.

14. A method as claimed in any one of claims 1 to 13, wherein the initiator is used in an amount within the range of from 0.01 to 1.0% by weight, based on the acrylate and silane.

15. A method as claimed in any one of claims 1 to 13, wherein the initiator is used in an amount within the range of from 0.05 to 1.0% by weight, based on the acrylate and silane.

16. A method as claimed in any one of claims 1 to 15, wherein the organic solvent is a hydrocarbon or a halogenated hydrocarbon.

17. A method as claimed in any one of claims 1 to 16, wherein the solvent is used in such an amount as to give a solution containing a total of from 5 to 60% by weight of the acrylate and the silane, based on the total weight of the reactants and solvent.

18. A method as claimed in any one of claims 1 to 16, wherein the solvent is used in such an amount as to give a solution containing a total of from 10 to 50% by weight of the acrylate and the silane, based on the total weight of the reactants and solvent.

19. A method as claimed in any one of claims 1 to 18, wherein the acrylate and the silane are used in a molar ratio within the range of from 1:99 to 99:1.

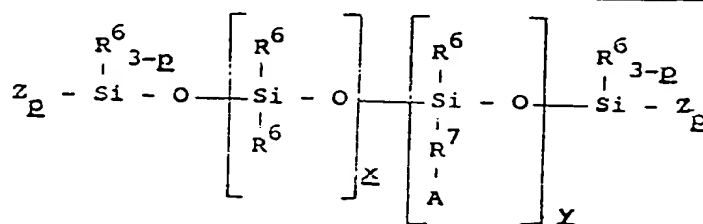
20. A method as claimed in any one of claims 1 to 18, wherein the acrylate and the silane are used in a molar ratio within the range of from 5:95 to 95:5.

21. A method as claimed in any one of claims 1 to 20, wherein the acrylate and the silane are reacted at a temperature within the range of from 50 to 150°C.

22. A method as claimed in any one of claims 1 to 21, wherein the acrylate and the silane are reacted at such a temperature that the initiator has a half-life within the range of from 15 min to 10 h.

23. A method as claimed in any one of claims 1 to 21, wherein the acrylate and the silane are reacted at such a temperature that the initiator has a half-life within the range of from 1 to 6 h.

24. A method as claimed in any one of claims 1 to 23, wherein the organopolysiloxane composition comprises an organopolysiloxane of the general formula



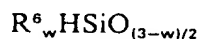
in which R⁶ denotes a monovalent hydrocarbon or halogenohydrocarbon radical having up to 18 carbon atoms or a cyanoalkyl radical, R⁷ denotes a divalent hydrocarbon or halogenohydrocarbon radical having up to 18 carbon atoms, A denotes an organic polymeric radical, Z denotes a hydroxy group or a group hydrolysable by atmospheric moisture, p denotes 1, 2 or 3, x denotes zero or an integer up to 20 000, and y denotes zero or an integer up to 500, with the proviso that the sum x+y is not less than 10.

25. A method as claimed in any one of claims 1 to 23, wherein the organopolysiloxane composition is a one-component composition and comprises (i) an organopolysiloxane of the general formula given in claim 24; and (ii)(a) optionally if, in the general formula given in claim 24, Z denotes a hydrolysable group but essentially if Z denotes a hydroxy group, a silane cross-linking agent of the general formula



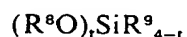
in which X denotes a group that is inert under the curing conditions, Y denotes a group hydrolysable by atmospheric moisture, and t denotes 3 or 4; and/or

(b) an organohydrogenopolysiloxane cross-linking agent of the average unit formula



in which R⁶ is defined as in claim 24 and w has a value between 0 and 2 exclusive.

26. A method as claimed in any one of claims 1 to 23, wherein the organopolysiloxane composition is a two-component composition and comprises (i) an organopolysiloxane of the general formula given in claim 24, in which Z denotes a hydroxy group; (ii) a cross-linking agent that is a (polyhydrocarboxy)silane of the general formula



or a partial hydrolysate thereof, or a (polyhydrocarboxy)siloxane in which any silicon valencies not satisfied by siloxane oxygen atoms are satisfied by a group denoted by R⁸O— or R⁹, in which formulae R⁸ denotes a monovalent hydrocarbon radical having up to 8 carbon atoms, R⁹ denotes a monovalent hydrocarbon or halogenohydrocarbon radical having up to 8 carbon atoms, and t denotes 3 or 4; and

(iii) a curing catalyst that is a carboxylic acid salt of lead, tin, zirconium, iron, cadmium, titanium, calcium or manganese.

27. A method as claimed in claim 1, carried out substantially as described in any one of Examples 1 to 7 and 10 herein.

28. An article comprising a porous substrate of a carbonaceous or masonry material to which a silicone elastomer has been bonded by a method as claimed in any one of claims 1 to 27.

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